Enhancement of anhydrous proton transport by supramolecular nanochannels in comb polymers

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Transporting protons is essential in several biological processes as well as in renewable energy devices, such as fuel cells. Although biological systems exhibit precise supramolecular organization of chemical functionalities on the nanoscale to effect highly efficient proton conduction, to achieve similar organization in artificial systems remains a daunting challenge. Here, we are concerned with transporting protons on a micron scale under anhydrous conditions, that is proton transfer unassisted by any solvent, especially water. We report that proton-conducting systems derived from facially amphiphilic polymers that exhibit organized supramolecular assemblies show a dramatic enhancement in anhydrous conductivity relative to analogous materials that lack the capacity for self-organization. We describe the design, synthesis and characterization of these macromolecules, and suggest that nanoscale organization of proton-conducting functionalities is a key consideration in obtaining efficient anhydrous proton transport.

fficient and selective transport of protons is critical both in biological contexts¹ and in materials for renewable energy². In biological systems, nature has optimized proton conduction on a nanometre scale by using secondary and tertiary structures of proteins to arrange precisely the appropriate side chains of amino acids, for example in the membrane protein M2 (refs 3–5). Although control of proton transfer on this scale is adequate for most biological processes, it is essential that efficient proton conduction be obtained on a micron scale for clean-energy applications^{6,7}.

In hydrogen fuel cells, for example, after oxidation of molecular hydrogen at the anode, the resulting protons must be transported across a selective membrane to reach the cathode and complete the conversion of chemical energy into electrical energy. The proton conductivity of this membrane, often called the protonexchange membrane or the polymer electrolyte membrane (PEM), has been one of the bottlenecks to achieving affordable fuel-cell technology. Nafion, a poly(tetrafluoroethylene)-based polymer with sulfonic acid groups arranged at intervals along the backbone, is one of the most widely used materials for this membrane⁸. The key to proton transport in Nafion is thought to be nanochannels of sulfonic acid groups, through which 'hydrated' protons can pass efficiently^{9–11}. Although a good proton conductor for hydrated protons, Nafion suffers from poor conductivity in unassisted proton transfer, that is Grotthuss or anhydrous proton transfer^{12,13}, which results in low conductivities at temperatures above the boiling point of water. PEMs with high proton conductivities at temperatures of 120-200 °C are desirable, because operation at higher temperatures can increase fuel-cell efficiency, reduce cost, simplify heat management and provide better tolerance of the catalysts against poisoning¹⁴.

One approach to address this issue is to use amphoteric functional groups that allow anhydrous proton transport^{15,16}, for example imidazole, which is a common motif in biological proton transport in the form of the amino acid histidine. Several groups have studied synthetic polymers that contain such amphoteric functional groups as candidates for high-temperature proton transfer^{17–22}. Although a number of interesting candidate materials were identified, one avenue that was not explored in these anhydrous proton-conducting systems is the role of supramolecular organization in nanoscale ion-conducting channels. This is surprising because, in the context of hydrated proton-conducting systems, such as Nafion⁹⁻¹¹ and sulfonated block copolymers^{12,23-26}, as well as lithium-ion conducting supramolecular assemblies^{27–29}, it is well-established that the formation of nanoscale domains enriched in the ion-conducting materials is critical to the resulting macro-scopic ionic conductivity.

In this paper, we describe the molecular design and synthesis of a novel class of comb polymers with amphoteric proton-transfer functionalities that can self-assemble into organized supramolecular structures. We also show that very subtle changes in the monomer and analogous polymer provide solid-state structures that lack such nanoscale organization. By comparing these polymers, we show that the self-assembled structures yield a dramatic increase in proton conductivity (by as much as three orders of magnitude), presumably because of the locally increased concentration of proton-transport functionalities within the nanophase-separated domains. These results suggest that a careful consideration of macromolecular architecture and nanoscale assembly is critical to optimizing anhydrous proton transport in new materials for PEMs.

Results

To prepare polymers that form supramolecular assemblies with proton-transporting functionalities concentrated within nanoscale domains, we made use of comb polymer architectures (Fig. 1). One of our groups recently used this architecture to prepare amphiphilic comb polymers by attaching lipophilic and hydrophilic functionalities at the meta-positions of the benzene ring of each styrenic repeat unit^{30,31}. Such polymers were shown to form assemblies of a micelle type in aqueous milieu and of an inverse-micelle type in apolar organic solvents. Thus, we hypothesized that similar polymers would also form nanoscale assemblies in the melt state. For this purpose, we designed a series of styrenic comb polymers in which one of the meta-positions contained a polar *N*-heterocyclic functionality capable of proton transport, and the other contained

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Figure 1 | **Structures and synthesis of benzotriazole-based polymers. a**, Benzotriazole-based polymers that only differ by the inclusion of a decyl chain. **b**, Synthetic scheme for benzotriazole-based polymers. This synthesis was modified slightly to prepare proton-conducting polymers without decyl chains and those that contain imidazole in place of benzotriazole. Details are given in the Supplementary Information. PCC = pyridinium chlorochromate.

a non-polar alkyl chain to drive phase segregation. For example, polymer 1 (Fig. 1a) contains non-conducting decyl chains and the proton-conducting heterocyclic functionality benzotriazole. Although Liu *et al.*¹⁸ reported that triazole appreciably enhances proton conductivities with respect to imidazole (also benzimidazole has been studied²⁰ as a proton-transporting functionality), we are not aware of any reports of benzotriazole used as a proton conductor. To test our premise that nanoscale phase segregation of 1 would facilitate proton transport, we synthesized the analogous polymer 2 that has no alkyl chains and therefore did not undergo nanoscale assembly. Syntheses of these polymers are exemplified with polymer 1 in Fig. 1b.

To determine proton-conductivity values, polymer films were drop-cast from solution onto a hole in a piece of Kapton tape and subsequently sandwiched between two electrodes to allow characterization by impedance spectroscopy, as described previously¹⁹. The Kapton tape determined the thickness of the polymer film, which was therefore constant at 125 μ m for all impedance measurements. Separate thermogravimetric analyses (TGAs) were conducted to verify that all polymers reported in this study were thermally stable up to at least 200 °C, which was the highest temperature investigated in the impedance measurements. Conductivities of the polymer samples were measured through several heating-cooling cycles (40–200 °C) under high vacuum and were found to be consistent from cycle to cycle, which eliminates any possible effects of residual solvent on the performance of these polymers.

Proton conductivities for 1 and 2 measured as a function of temperature between 40 and 200 $^{\circ}$ C are shown in Fig. 2a. Both polymers show qualitatively similar non-Arrhenius increases in conductivity with temperature that are typical for anhydrous proton-conducting polymers. However, the conductivity of 1 ranges

from 6×10^{-6} S cm⁻¹ at ambient temperature to 1.3×10^{-3} S cm⁻¹ at 200 °C, at least two orders of magnitude larger than the conductivity of **2** across the same temperature range, which varies from 4×10^{-9} S cm⁻¹ at ambient temperature to 1.2×10^{-5} S cm⁻¹ at 200 °C. As a benchmark, Nafion membranes show room-temperature conductivities of 10^{-2} to 10^{-1} S cm⁻¹ when fully hydrated³², but at low humidity (below 5%) their conductivities were reported as 10^{-7} to 10^{-5} S cm⁻¹ (ref. 33). (Under our experimental conditions, measured conductivities of Nafion were below the noise floor of the measurements of $\sim 10^{-9}$ S cm⁻¹.) Thus, although the conductivities of our materials remain significantly below those of Nafion under ideal conditions, the dramatic increase in conductivity from **2** to **1** suggests an important design principle for optimizing proton transport under anhydrous conditions.

At first, it may seem surprising that the addition of a decyl chain to each repeat unit of a polymer could boost proton conductivity by two orders of magnitude. After all, the average density of protontransporting groups is lowered by the presence of the decyl chain; the benzotriazole unit makes up only 23 weight per cent (wt%) of **1** as compared to 34 wt% of **2**. However, we hypothesized that the decyl chain renders the mixing of **1** with the amphoteric heterocycles incompatible, and so drives **1** to self-assemble and form nanoscale domains that contain enhanced local concentrations of benzotriazole, and thereby facilitates proton transport.

To test this hypothesis, we characterized the structures of these polymers using small-angle X-ray scattering (SAXS). As shown in Fig. 2b, polymer 1 gave rise to scattering peaks that indicate self-assembled nanostructures, but the control polymer 2 yielded a completely featureless pattern that indicates a homogeneous phase-mixed structure. The first-order scattering peak from 1 falls at $q^* = 1.47$ nm⁻¹, which corresponds to a real-space



Figure 2 | **Conductivity and SAXS results for benzotriazole polymers. a**, Proton conductivity over a wide temperature range, in which the polymer that contains the decyl chain exhibits a much higher conductivity than that of its counterpart. **b**, SAXS profiles of benzotriazole polymers that indicate ordering of the alkylated polymer. Curves are shifted vertically for clarity. *I*(**q**) is the azimuthally-averaged scattering intensity as a function of scattering wave-vector (*q*). **c**, An illustration of the proposed structure of **1**, with two units arranged with the benzotriazoles head-to-head, which thus allows for hydrogen bonding. a.u. = arbitrary units.

distance of d = 4.3 nm, and a faint, although clearly resolvable, second-order peak at $\sqrt{4q}^*$. Although the structure cannot be determined unambiguously from these data, the presence of only a second-order peak suggests a lamellar structure with a repeat spacing of 4.3 nm. We estimate the fully stretched length of a monomer, from the tip of the decyl chain to the benzotriazole group, as ~ 3 nm, and thus the observed repeat spacing is consistent with 'back-to-back' stacking of polymer chains with some interdigitation of the decyl chains and/or benzotriazole group and spacer. A schematic of this proposed structure is shown in Fig. 2c, in which two repeating units arranged with the benzotriazoles head-to-head allow hydrogen bonding, with the alkyl groups pointed away from each other. Analysis of the first-order peak revealed a width (full-width

at half-maximum, Δq) of 0.6 nm⁻¹ for polymer 1, which yielded a correlation length of $2\pi/\Delta q \approx 10$ nm, indicating that the size of ordered domains is small, with positional correlations that extend only over several repeat units.

As demonstrated by Ikkala and co-workers³⁴, self-assembly into anisotropic nanostructures yields orientation-dependent conductivity, and McGrath and co-workers have shown that continuity of nanoscale domains is critical to efficient proton transport in sulfonated polymers³⁵. For our polymers, although the limited length of ordering precludes any considerations of the effects of orientation or dimensionality of nanoscale domains on conductivity, the nanoscale organization provided by supramolecular assembly clearly enhances anhydrous proton conductivity by at least two orders of magnitude

Table 1	Properties of	f polymers	1, 2, 7 and 8.
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Polymer	Decomposition onset (°C) (5% weight loss)	T _g (°C)	N-heterocycle weight fraction (%)	Molecular weight (Mn)
1	218	55	23	25,000
2	233	67	34	25,000
7	225	61	14	23,000
8	221	71	20	24.000

Glass-transition temperatures, decomposition onset temperatures, N-heterocycle weight fractions and molecular weight of polymers 1, 2, 7 and 8. Mn = number-average molecular weight.

compared with that of the phase-mixed control polymer. The exact mechanism of enhancement is currently unclear, although we speculate that self-organization leads to interconnected channels of locally enriched benzotriazole concentrations that facilitate proton hopping through the membrane. To test for the possibility of disordering or nanoscale structural transitions at high temperature (which, in some cases, have yielded dramatic changes in ionic conductivity²⁷), we carried out variable-temperature SAXS measurements over the range 40–200 °C. Although the intensity of the

first-order scattering peak decreased continuously with increasing temperature, its position and width remained nearly constant, which indicates that a similar level of nanoscale organization was present in these materials over the entire temperature range of interest (see Supplementary Information for details).

An additional factor to consider when the proton conductivities of two polymer chains that bear the same functional group are compared is the glass-transition temperature (T_{a}) , because the mobility of the polymer chain is well-known to influence the rate of proton transport³⁶. To test whether the difference in conductivity observed between 1 and 2 simply reflects a decrease in T_{o} because the decyl chain is present, we carried out differential scanning calorimetry experiments. As summarized in Table 1, the T_{o} values of 1 and 2 were 55 °C and 67 °C, respectively. The modest difference in T_g between these polymers suggests that the mobility of the polymer backbone is not a major contributor to the difference in proton conductivities observed. As relatively high conductivity values of 1 were achieved at temperatures well above $T_{\rm g}$, the mechanical properties of this polymer at such temperatures are not well-suited for application as PEMs. Although components with higher $T_{\rm g}$ values or semicrystalline components need to be incorporated to provide materials

Figure 3 | **Results for imidazole-based polymers a**, Structures of imidazole polymers that only differ by the inclusion of a decyl chain. **b**, Proton conductivity over a wide temperature range, which again demonstrates that the polymer with an added decyl chain has a much higher conductivity. **c**, SAXS profiles of imidazole polymers, which show order in polymer **7** and a disordered polymer **8**. Curves are shifted vertically for clarity. **d**, An illustration of the proposed structure of **7**, which self-assembles into cylindrical domains.

with adequate mechanical properties, we emphasize that the polymers described here provide proof-of-concept results and demonstrate the importance of nanoscale organization in anhydrous proton conductivity.

If our hypothesis and conclusions are correct, this molecular design strategy should also work for other amphoteric heterocycles. To test the generality of our molecular design, we prepared polymers that contained imidazole as a proton-transporter functionality, which was also shown to be capable of anhydrous proton transfer^{16–19} and has a very different dissociation constant (pK_a) value in the protonated form as compared to that of benzotriazole. In analogy to 1 and 2, we synthesized polymers 7 and 8 with imidazole moieties (Fig. 3a). Alternating current impedance measurements revealed that polymer 7, with its decyl chain, exhibits dramatically higher conductivity than that of the corresponding control polymer 8, in this case by more than three orders of magnitude (Fig. 3b). The morphologies of these polymers were investigated using SAXS and revealed that 7 gave two well-defined scattering peaks, which indicates the presence of self-assembled nanostructures, but 8 showed no signs of structure (Fig. 3c). The second scattering peak for 7 falls at a position of $\sqrt{3q^*}$, which clearly indicates a non-lamellar structure and suggests a hexagonal symmetry that probably corresponds to a structure of hexagonally packed cylinders (Fig. 3d). T_{α} values determined for these polymers (Table 1) are very similar, which once again reveals that mobility of the polymer backbone is not a significant factor in the difference in proton conductivity of three orders of magnitude. We also tested random copolymers synthesized from a monomer disubstituted with decyl groups and another monomer disubstituted with N-heterocycles (1:1 ratio). These random copolymers also provided some extent of phase separation, but with nanostructures organized more poorly than those of the comb polymers and with only a single scattering peak for each. The conductivities of these random copolymers are generally significantly greater than those of the unorganized control homopolymers 2 and 8, although somewhat less than those of the comb polymers 1 and 7 (see Supplementary Information). This further supports our conclusion that phase separation on a nanoscale is tied directly to the efficiency of proton transport.

In summary, we have designed, synthesized and characterized a new class of comb polymers for anhydrous proton transport. We have shown that:

- styrenic comb polymers that contain incompatible functionalities at opposite faces of the monomer units provide ordered nanostructures through self-assembly in the melt state;
- styrenic polymers that contain a non-conducting decyl group and a proton-conducting functionality on the meta-positions of the phenyl ring exhibit conductivities two-to-three orders of magnitude greater than those of polymers that contain only the conducting functionality, despite the lower overall content of proton transporter in the former;
- polymer backbone mobility is not a major contributor to the observed differences in proton conductivity in these systems;
- the high conductivities observed for the decyl-functionalized polymers correlate with the ability to form organized lamellar or hexagonal nanostructures that consist of domains with locally high concentrations of proton conductors that facilitate transport;
- this molecular design strategy works for two different protontransfer functionalities with substantially different pK_a values, which suggests that the importance of nanochannel formation in proton conduction is a general phenomenon.

Our work here indicates that careful consideration of polymer architecture and nanoscale morphology is a key element in the design of efficient anhydrous PEMs.

Methods

TGA was carried out using a TA Instruments TGA 2950 thermogravimetric analyser with a heating rate of 10 $^\circ\rm C$ min $^{-1}$ from room temperature to 500 $^\circ\rm C$ under nitrogen.

Glass-transition temperatures were obtained by differential scanning calorimetry using a TA Instruments Dupont DSC 2910. Samples were analysed at a heating rate of 10 $^{\circ}$ C min⁻¹ from 0 $^{\circ}$ C to 150 $^{\circ}$ C under a flow of nitrogen (50 ml min⁻¹).

Electrochemical impedance data were obtained using a Solartron 1287 potentiostat and 1252A frequency response analyser in the range 0.1 Hz to 300 kHz. Measurements were conducted under vacuum at temperatures between 40 °C and 200 °C with a sinusoidal excitation root-mean-square voltage of 0.1 V. The sample thickness and contact surface area were controlled by a 125 μ m thick Kapton tape with a 0.3175 cm diameter hole.

SAXS measurements were carried out on an in-house beamline using a Rigaku rotating anode source to generate Cu K_{α} radiation (wavelength $\lambda=0.154$ nm). Scattering patterns were collected on an image plate positioned a distance of 500 mm from the sample. All samples yielded isotropic patterns, and thus data were integrated to yield plots of intensity as a function of the magnitude of the scattering vector, $q=(4\pi/\lambda)\sin(\theta)$, where 2θ is the total scattering angle. The actual scattering angles were calibrated using the known reflection from silver behenate.

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Author contributions

S.T. and Y.C. conceived the molecular design. S.T., R.H. and Mark T. planned the project. Y.C, Michael T., S.C. and C.V. carried out the experiments and analysed the data. Y.C. and A.P. synthesized the discussed compounds, Michael T. and C.V. measured ionic conductivities, and S.C. performed SAXS. Results were discussed by R.H., Mark T. and S.T. All authors contributed to writing the manuscript.

Additional information

The authors declare no competing financial interests. Supplementary information and chemical compound information accompany this paper at www.nature.com/ naturechemistry. Reprints and permission information is available online at http://npg.nature. com/reprintsandpermissions/. Correspondence and requests for materials should be addressed to R.C.H., M.T.T. and S.T.